



Effects of heating rate on slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo



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HIGHLIGHTS

- Biochar and bio-oil decrease while gas yield increases with increasing heating rate.
- Activation energy values for bamboo pyrolysis increase with increasing heating rate.
- Increasing heating rate improves phenolics production while reduces water in bio-oil.
- Temperature gradient and secondary decomposition are noticeable in fixed bed reactor.
- Increasing heating rate improves the specific surface area of the biochar.

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ABSTRACT

Effects of heating rate on slow pyrolysis behaviors, kinetic parameters, and products properties of moso bamboo were investigated in this study. Pyrolysis experiments were performed up to 700 °C at heating rates of 5, 10, 20, and 30 °C/min using thermogravimetric analysis (TGA) and a lab-scale fixed bed pyrolysis reactor. The results show that the onset and offset temperatures of the main devolatilization stage of thermogravimetry/derivative thermogravimetry (TG/DTG) curves obviously shift toward the high-temperature range, and the activation energy values increase with increasing heating rate. The heating rate has different effects on the pyrolysis products properties, including biochar (element content, proximate analysis, specific surface area, heating value), bio-oil (water content, chemical composition), and non-condensable gas. The solid yields from the fixed bed pyrolysis reactor are noticeably different from those of TGA mainly because the thermal hysteresis of the sample in the fixed bed pyrolysis reactor is more thorough.

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1. Introduction

Bamboo is a very potential renewable biomass with the advantages of short growth cycle and high yield (Jiang et al., 2012). The bamboo resource is extremely abundant in China, covering about 50,000 km² of the land and accounting for 1/10 of the woody material market (Xiao et al., 2007). For a long period, bamboo is mainly used for bamboo charcoal production, which is traditional bamboo utilization through extremely slow carbonization. In the past decade, the thermochemical utilization of biomass has gained widespread attention (Bridgwater, 2012). Bamboo, as an important biomass material, can be converted into valuable biofuels and chemicals (Kantarelis et al., 2010). Pyrolysis is the basis of thermochemical processes. Therefore, investigating the pyrolysis

properties of bamboo is exceptionally helpful in understanding the conversion process and in making bamboo a bio-energy resource for gas, biofuel, and char production.

The pyrolysis characteristics of bamboo have been previously studied, which mainly focused on the rapid pyrolysis of bamboo (Kantarelis et al., 2010; Lou et al., 2010a; Lou et al., 2010b; Muhammad et al., 2012; Mun and Ku, 2009; Ren et al., 2013). Few studies have examined the slow pyrolysis of bamboo. Xiao et al. studied bamboo pyrolysis through thermogravimetric analysis (TGA), and the main reaction was found to occur at 250–400 °C. The solid products yield slowly decreased from 25% to 17% when the temperature increased from 400 °C to 700 °C (Xiao et al., 2007). Mui et al. studied bamboo pyrolysis kinetics based on three main bamboo components using the Runge–Kutta mechanism. The results showed that either the three- or the six-component model was preferred in describing bamboo pyrolysis (Mui et al., 2008). Jiang et al. studied the pyrolysis characteristics of moso bamboo

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using thermogravimetry-Fourier transform infrared (TG–FTIR), and found that the pyrolysis of moso bamboo included three stages. Main pyrolysis occurred in the second stage, wherein the temperature ranged from 450 K to 650 K, and over 68.69% mass was degraded. The TG–FTIR analysis showed that the main pyrolysis products absorbed were water (H₂O), methane gas (CH₄), carbon dioxide (CO₂), acids and aldehydes (Jiang et al., 2012). Ren et al. calculated the kinetic parameters of moso bamboo pyrolysis using a 3D diffusion model, and found that raw moso bamboo had an activation energy of 164.3 kJ mol^{−1} (Ren et al., 2013). These previous studies achieved remarkable advances in understanding the thermal decomposition of bamboo. However, the behavior and distribution of the products of moso bamboo pyrolysis, especially the properties of the pyrolysis products at different heating rates, have not been fully investigated. Heating rate, a key pyrolysis parameter, has a significant effect on biomass pyrolysis (Angin, 2013; Mohanty et al., 2013). Therefore, the present research first determines the effects of heating rate on bamboo pyrolysis behavior and kinetics using TGA.

TGA has the advantages of minimal material requirement, precise temperature control, and online recording of experimental data (Chen et al., 2012). It has been widely used to detect the mass loss of biomass and analyze the pyrolysis properties. But it cannot be used to collect and determine the solid, liquid, and gaseous products of pyrolysis. TGA is therefore unsuitable for studying the effect of heating rate on the products of bamboo pyrolysis. From the literature point of view, few experimental studies have been conducted on product properties of bamboo pyrolysis. Thus, pyrolysis experiments were performed in this research using a lab-scale fixed bed pyrolysis reactor at different heating rates. The properties of gaseous, liquid, and solid products were analyzed to obtain more information on bamboo.

The objectives of the present study are to determine the effect of heating rate on pyrolysis behaviors, kinetics, as well as gaseous, liquid, and solid products of moso bamboo, and to provide a theoretical basis for bamboo utilization.

2. Methods

2.1. Raw material

Moso bamboo is the most abundant kind of bamboo in China. Moso bamboo (*Phyllostachys edulis*), collected from xiashu internship forest farm of Nanjing forestry university, was used as the raw material in this study. Before the test, moso bamboo was screened into a particle size of 40–60 mesh, and then dried for 6 h at 110 °C.

2.2. Thermogravimetric analysis

Thermogravimetric analysis of moso bamboo was performed using a thermogravimetric analyzer (TGA Q500, TA Instruments, USA). For each experiment, about 10 mg of the material was used and a nitrogen flow rate of 100 ml/min was adopted. To eliminate moisture effect on pyrolysis, the material was first heated from room temperature to 100 °C and kept for 1 min. Then the material was heated to 700 °C at different heating rates of 5, 10, 20, and 30 °C/min. All experiments were replicated three times at each heating rate and averages of weight loss were used.

2.3. Kinetics analysis

The Coats–Redfern model is one of the most common models successfully used in the kinetics study of biomass decomposition. In this study, this model was used to calculate the kinetics

parameters at each of heating rates, and to study the heating rate on the activation energy.

The final form of Coats–Redfern model can be generally described as follows.

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E_a} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT} \quad (1)$$

where E_a is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/K mol), A is the pre-exponential factor (min^{−1}), T is the absolute temperature (K), β is the heating rate. α is pyrolysis transformation rate which can be calculated by

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (2)$$

where m , m_0 and m_∞ were time t , initial and final weight of the sample, respectively.

Since $E_a/RT > 1$, $\ln [AR/\beta E_a(1 - 2RT/E_a)] \approx \ln [AR/\beta E_a]$ is nearly constant. Thus, a plot of the left side of Eq. (1) against $1/T$ should be a straight line with a slope $-E_a/R$ and an intercept of $\ln(AR/\beta E_a)$ from which the E_a and A can be obtained. The criterion used for accepted values of E_a and A is that the straight line should be given with high correlation coefficient.

The modified Coats–Redfern method is a multiple-heating rate application of the Coats–Redfern equation. The form of modified Coats–Redfern model can be generally described as follows (Jiang et al., 2012).

$$\ln \left[\beta / \left(T^2 (1 - 2RT/E_a) \right) \right] = \ln [-AR/(E_a \ln(1 - \alpha))] - E_a/RT \quad (3)$$

In the study, the modified Coats–Redfern methods were used to determine the E_a value as a function of conversion. Plotting the left hand side of Eq. (3) for each heating rate versus $1/T$ at that heating rate gave a series of straight lines having slope $(-E_a/R)$. The full solution was to be done iteratively by first assuming E_a value and then recalculating the left hand side until convergence occurs. Here, a quick solution, however, was also available by moving $(1 - 2RT/E_a)$ into the intercept and assuming that it was a constant (Jiang et al., 2012).

2.4. Experiments in a lab-scale fixed bed pyrolysis reactor

Slow pyrolysis experiments of moso bamboo were performed in a lab-scale fixed bed pyrolysis reactor which is shown in Fig. 1. Before the experiment, about 50 g sample was placed in the pyrolysis furnace. High purity nitrogen (>99.999%) gas was used to purge and exhaust the air inside the furnace. Then, open the temperature controller and start experiments according to the settled heating rate. Thermocouple was inserted into the sample inside, and the sample temperature was recorded every two minutes. Moso bamboo was heated from room temperature to 700 °C at different heating rates of 5, 10, 20, and 30 °C/min. The liquid product (bio-oil) was condensed in the condenser (Cooling medium: liquid ethanol, about −35 °C), and the non-condensable gas was collected in a gas bag. After the experiment, the solid product (biochar) was collected for further analysis.

2.5. Properties analysis

Proximate analysis of sample was performed according to the ASTM D3172-07a standard practice. Ultimate analysis of sample was carried out using an elemental analyzer (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference. Due to the water in bio-oil has a significant influence on the analysis results, the ultimate analysis results of biochar and bio-oil were reported in this study basing on the dry basis. The higher heating values (HHV) of biochar and bio-oil were measured in an

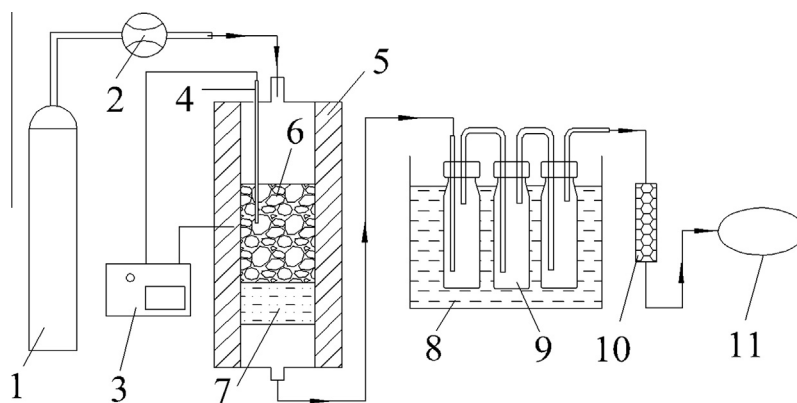


Fig. 1. Illustration of the lab-scale fixed-bed pyrolysis reactor. (1) nitrogen supplier, (2) flowmeter, (3) temperature controller, (4) thermocouple, (5) pyrolysis furnace, (6) feedstock, (7) silica wool, (8) condenser, (9) bio-oil collector, (10) drier, (11) gas bag.

adiabatic oxygen bomb calorimeter (XRY-1A, Changji Geological Instruments, China). The textural properties of biochar were performed using an automatic surface area and pore analyzer (Quadrasorb SI, Quantachrome, USA). The specific surface area was calculated according to Brunauer–Emmett–Teller (BET) equation at a relative pressure of 0.05–0.2. The water content in bio-oil was analyzed by Karl-Fischer titration according to ASTM D.1744. The viscosity of bio-oil was measured at 40 °C using 0.8 mm diameter tube by a petroleum products kinematic viscosity meter (SYD-265, Shanghai Jichang, China). Composition analysis of bio-oil was carried out using a gas chromatography/mass spectrometry (GC/MS 7890A/5975C, Agilent Company, USA). The non-condensable gas was detected by a gas chromatograph analyzer (GC-TCD 7890 II, Shanghai Tianmei, China).

3. Results and discussion

3.1. Effect of heating rate on pyrolysis using TGA

3.1.1. Thermogravimetric analysis

The results of the thermogravimetric experiments at the heating rates of 5, 10, 20, and 30 °C/min are presented in Fig. 2. It can be observed that pyrolysis process of moso bamboo consists of different stages. These results are similar to other biomass reported in the literature (Chen et al., 2011). Cellulose, hemicellulose and lignin are the main components in bamboo and their percentages are 35–45%, 15–20% and 15–25%, respectively (Xiao et al., 2007). These components behave differently during pyrolysis (Yang et al., 2007). Hemicellulose has high activity in thermal decomposition attributed to its unfixed structure with short molecular chains and many branches. In contrast, cellulose is a highly linear, non-branching polymer formed by D-glucose, leading to a higher thermal stability. Lignin is full of aromatic rings and is heavily cross-linked. Thus, lignin is difficult to decompose. In main temperature range of decomposition for hemicelluloses, cellulose and lignin are 200–380 °C, 250–380 °C, and 180–900 °C, respectively (Chen et al., 2013). As a result, the former shoulder peak in the DTG curves results from the devolatilization of hemicellulose, whereas the latter main peak results from the devolatilization of cellulose.

3.1.2. Effect of heating rate on TG/DTG curves

Heating rate is a key parameter in the pyrolysis of biomass. The onset and offset temperatures of the main devolatilization stage shift obviously toward the high-temperature range as the heating rate rises. Previous studies have attributed this phenomenon to heat and mass transfer limitations (Güldoğan et al., 2002; Haykiri-Acma et al., 2006; Mani et al., 2010). This means that

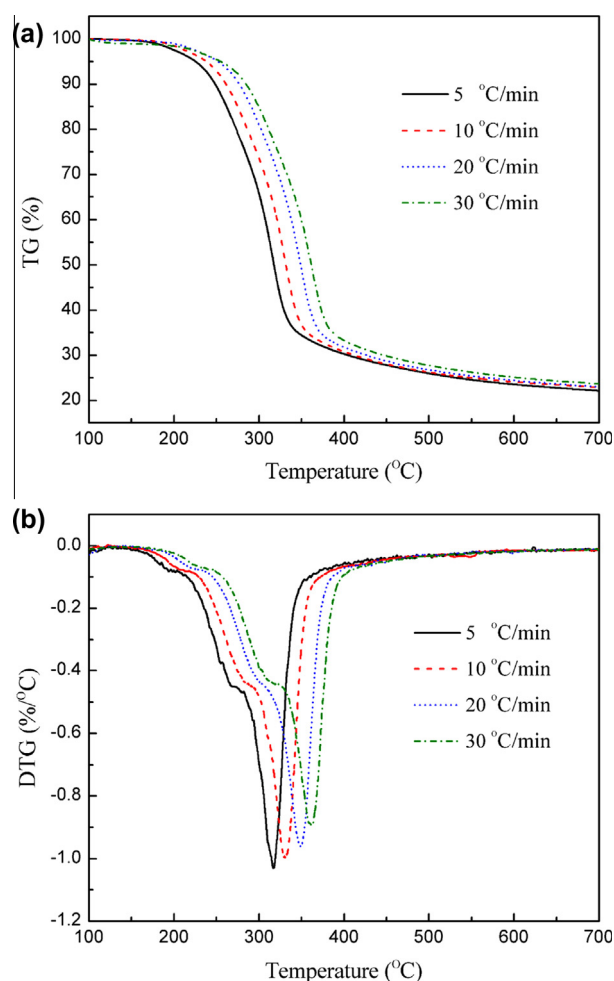


Fig. 2. TG/DTG curves of moso bamboo at different heating rates of 5, 10, 20, and 30 °C/min.

temperature gradients may exist in sample, and the devolatilization rate is faster than the volatile release. Thus, different devolatilization stages take place. For this reason, small particle size of the sample with uniform distribution is accepted in TG experiments.

The bamboo pyrolysis residues (i.e., biochar) yields at different heating rates obtained from TGA are very close, which range from 21.3% at 5 °C/min to 22.6% at 30 °C/min. This 1% change suggests that the range is not large enough to see measurable difference.

Previous studies also showed that heating rate did not have obvious and consistent effects on the biochar yield of bamboo in TGA. Oyedun et al. found that the residues yields increased with increasing heating rate (Oyedun et al., 2013); but the data of residues yields were very close. Whereas, in the study of Wang et al., the residues yields of bamboo at different heating rates were found to be $10\text{ }^{\circ}\text{C}/\text{min} > 20\text{ }^{\circ}\text{C}/\text{min} > 30\text{ }^{\circ}\text{C}/\text{min} > 5\text{ }^{\circ}\text{C}/\text{min}$ (Wang et al., 2013). Therefore, heating rate's impact is very limited in this case.

3.1.3. Effect of heating rate on kinetic parameters

Table 1 shows the calculation results including the values for E_a and A by Coats–Redfern method. The activation energy values of the samples vary ranging from 75.3 to 98.7 kJ/mol. In particular the relationship between the heating rates and the kinetic parameters, derived from the Arrhenius plots in this study, increased with heating rate. Similar results were observed in cellulose, hemicellulose, lignin (Mui et al., 2008) and coal (Guo et al., 2013). For this phenomenon, Mui et al. gave an explanation that more reactions were triggered simultaneously at higher heating rates, leading to a sharp rise in reaction rates with more unstable radicals/intermediates and lower activation energies; and then these values were incorporated into the kinetic equations as initial guess values and further optimized (Mui et al., 2010).

3.1.4. The relationship between activation energy and conversion rate

The typical plots of the modified Coats–Redfern are shown in Fig. 3. It can be seen that the fitted lines were nearly parallel at conversion rate from 0.1 to 0.75, which indicated approximate E_a values at different conversions and consequently implied the possibility of single reaction mechanism. The E_a values of moso bamboo calculated according to the conversion rate using the modified Coats–Redfern methods are listed in Fig. 3. The E_a values of moso bamboo were around 96.3–113.2 kJ/mol at conversion rate from 0.1 to 0.75. Jiang et al. noted that the information of activation energy vs. conversion rate was very helpful for designing manufacturing process of bio-energy, made from moso bamboo, using gasification or pyrolysis (Jiang et al., 2012).

The activation energy changed with increasing conversion, which can be attributed to the different pyrolysis characteristics of the three components of biomass. Cellulose is a semi-crystalline material, while lignin and hemicellulose are non-crystalline, so the decomposition of cellulose must first destroy the lattice structure of cellulose which needs extra energy, leading to its much higher activation energy than for hemicellulose and lignin. Previous study has shown that the activation energies for cellulose, hemicelluloses, and lignin are in the range of 145–285, 90–125, and 30–39 kJ/mol, respectively (Vamvuka et al., 2003). Therefore, the different pyrolysis behaviors of the three components in moso bamboo led to the activation energy as a function of the conversions. Similar results were reported for wood (Shen et al., 2011) and agricultural wastes (Chen et al., 2013).

3.2. Effect of heating rate on pyrolysis products

3.2.1. Evaluation of non-isothermal condition

Biomass pyrolysis is a complicated heat and mass transfer process. For TG analysis, only about 10 mg of moso bamboo samples were used. The endothermic and exothermic effects of the sample

Table 1
Effect of heating rate on kinetic parameters using Coats–Redfern method.

Heating rate ($^{\circ}\text{C}/\text{min}$)	E_a (kJ/mol)	A (min^{-1})	R^2
5	75.3	1.23×10^5	0.9768
10	77.6	1.25×10^5	0.9812
20	86.2	2.13×10^5	0.9920
30	98.7	3.37×10^5	0.9805

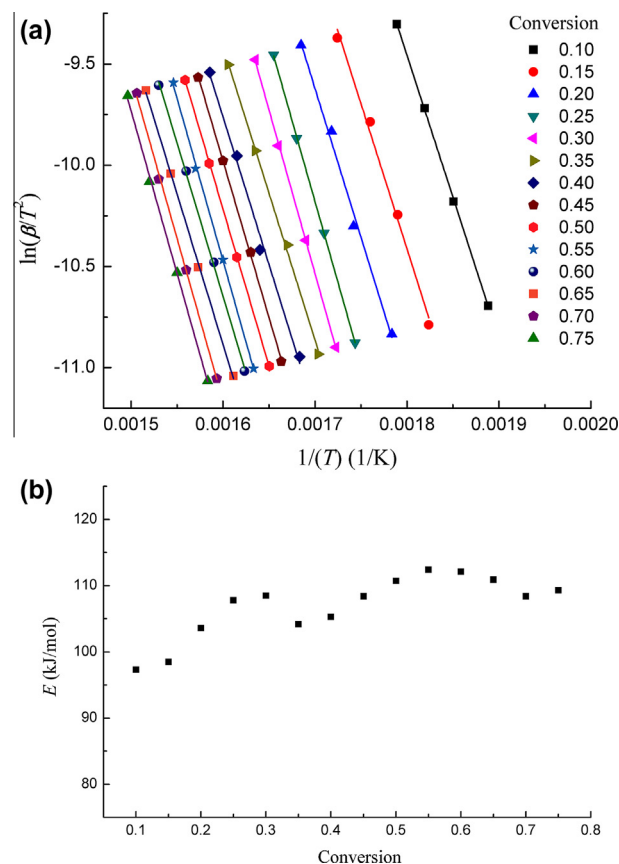


Fig. 3. Multiple-heating rate application in kinetics analysis: (a) the typical plot of modified Coats–Redfern for moso bamboo; (b) the relationship between activation energy and conversion rate.

exerted minimal effect on furnace temperature, so the linear heating rate of the sample was easily achieved. While, the sample in the fixed bed pyrolysis reactor was about 50 g. The heating effect of the sample on the environment cannot be ignored, and thus the sample temperature is not easily ensured as programmed. Fig. 4 shows the temperature profiles of the bamboo samples in the fixed bed pyrolysis reactor. It can be observed that the non-isothermal conditions were basically established and the sample was heated at approximate constant heating rate.

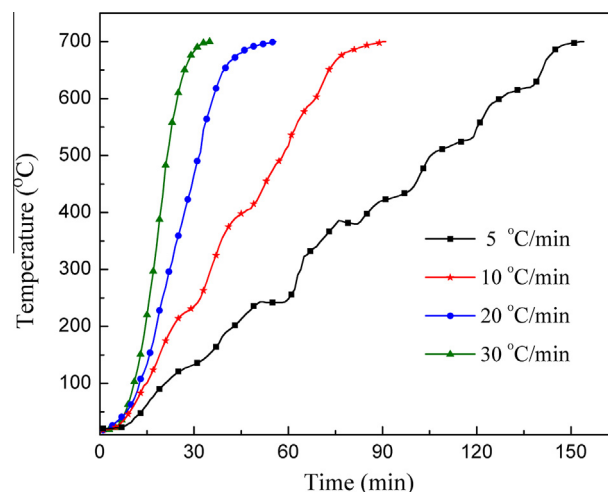


Fig. 4. Temperature profiles of the bamboo samples at different heating rates in the lab-scale fixed bed pyrolysis reactor.

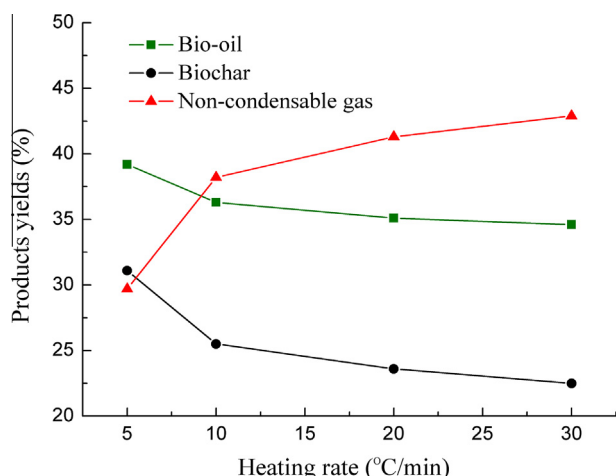


Fig. 5. Effect of heating rate on products yields of moso bamboo pyrolysis.

3.2.2. The yields of pyrolysis products

The biochar and bio-oil collected after the test were collected and weighed to determine the yields. The non-condensable gas yield was calculated by difference. The products yields of slow pyrolysis at different heating rates are shown in Fig. 5. It can be seen that the heating rate within the scope of 5–30 °C/min have important effects on bamboo products yields. With increasing heating rate, biochar yield obviously decreases from 31.1% at 5 °C/min to 22.5% at 30 °C/min and bio-oil yield decreases from 39.2% at 5 °C/min to 34.6% at 30 °C/min, whereas non-condensable

gas yield increases from 29.7% at 5 °C/min to 42.9% at 30 °C/min. In addition to the heating rate, there are some other pyrolysis factors such as volatiles residence time. The relatively long residence time of volatiles in the fixed bed pyrolysis reactor improved second cracking and increased the opportunity reaction with biochar, which had an important influence the product yields and characteristics.

The results obtained from the fixed bed pyrolysis reactor are obviously different from those of TGA: (i) the biochar yields obtained from the fixed bed pyrolysis reactor ranging from 25.5% to 36.1% are obviously higher than those from TGA which range from 21.3% to 22.6%; (ii) the biochar yield significantly changes in the fixed bed pyrolysis reactor, whereas it barely changes in TGA; (iii) the biochar yields in the fixed bed pyrolysis reactor decreases with increasing heating rate, whereas no obvious change trend is found in TGA. These results are mainly due to the thermal hysteresis of the 50 g bamboo material in the fixed bed pyrolysis reactor, which is more thorough than that of the 10 mg material in TGA. The bamboo stays in the same temperature period for a longer time at lower heating rates, and thus the carbonization

Table 4

Effect of heating rate on non-condensable gas properties.

Heating rate (°C/min)	Volume percentages (%)			
	CO ₂	H ₂	CH ₄	CO
5	35.67	25.14	11.86	20.11
10	33.94	27.75	10.59	22.03
20	36.08	22.61	15.09	18.21
30	33.72	24.85	12.75	22.35

Table 2

Effect of heating rate on the basic properties of bio-oil.

Heating rate (°C/min)	Ultimate analysis (% db)					Water content (%)	pH	Viscosity at 40 °C (mm ² /s)
	C	H	O	N	S			
5	69.3	6.1	22.7	1.6	0.3	68.5	2.5	1.168
10	67.5	6.1	24.3	1.9	0.2	69.5	2.6	1.026
20	70.4	5.8	21.5	2	0.3	65.4	2.8	1.172
30	65.5	6.3	26.1	1.8	0.3	62.8	2.8	1.210

Table 3

Identified pyrolytic products from slow pyrolysis at different heating rates (°C/min) of moso bamboo.

No.	Compound	Formula	Yield, percent of peak area (%)			
			5	10	20	30
1	Methyl formate	C ₂ H ₄ O ₂	1.39	1.13	1.45	0.86
2	Acetic acid	C ₂ H ₄ O ₂	7.96	8.61	8.10	6.63
3	Hydroxyacetone	C ₃ H ₆ O ₂	0.84	0.45	0.71	0.68
4	Propionic acid	C ₃ H ₆ O ₂	0.18	0.27	0.23	0.23
5	1-Hydroxy-2-butanone	C ₄ H ₈ O ₂	1.98	1.08	2.97	1.35
6	Cyclopentanone	C ₅ H ₈ O	7.86	6.50	8.48	6.52
7	Furan	C ₄ H ₄ O	4.83	5.03	4.12	5.13
8	Butyrolactone	C ₄ H ₆ O ₂	6.15	6.54	6.09	5.01
9	Furfuryl alcohol	C ₅ H ₆ O ₂	0.44	0.03	0.26	0.23
10	Phenol	C ₆ H ₆ O	4.21	5.33	5.44	6.23
11	Guaiacol	C ₇ H ₈ O ₂	1.28	1.31	1.81	1.89
12	3-Methyl-1,2-cyclopentanedione	C ₆ H ₈ O ₂	1.58	1.35	1.55	1.33
13	2,3-Dihydrobenzofuran	C ₈ H ₈ O	1.01	0.70	0.92	0.89
14	3-methyl phenol	C ₇ H ₈ O	7.93	8.71	8.20	8.73
15	4-Methoxyphenol	C ₇ H ₈ O ₂	3.20	2.64	2.88	3.01
16	Vanillin	C ₈ H ₈ O ₃	1.35	1.09	1.32	1.37
17	2-Methoxy-4-methyl Phenol	C ₈ H ₁₀ O ₂	3.00	3.01	2.76	3.15
18	Isoeugenol	C ₁₀ H ₁₂ O ₂	1.31	1.05	1.56	1.83
19	2,6-Dimethoxyphenol	C ₈ H ₁₀ O ₃	5.40	6.09	5.81	7.82
20	1,2,4-Trimethoxybenzene	C ₉ H ₁₂ O ₃	3.36	3.23	3.16	3.04
21	3,5-Dimethoxyacetophenone	C ₁₀ H ₁₄ O ₃	1.73	1.53	1.42	1.70

Table 5

Proximate analysis, ultimate analysis, heating value and specific surface area of moso bamboo and biochar.

Sample	Ultimate analysis (% db)					Proximate analysis (% db)			Heating value (MJ/kg)	Specific surface area (m ² /g)
	C	H	O	N	S	Fixed carbon	Volatiles	Ash		
<i>Moso bamboo</i>	47.58	6.13	45.73	0.52	0.04	13.32	85.53	1.15	16.85	
<i>Biochar obtained at different hearing rates (°C/min)</i>										
5	88.12	1.17	9.54	1.03	0.14	88.52	6.56	4.92	28.02	64.32
10	89.71	1.19	7.91	1.05	0.14	89.84	5.27	4.89	28.25	64.78
20	87.23	1.13	10.34	1.16	0.14	89.04	4.45	6.51	27.76	69.56
30	85.94	0.87	11.86	1.21	0.12	87.58	3.26	9.16	27.29	72.63

degree is higher, leading to higher biochar product at the end of experiment. Some previous studies have also shown that slower pyrolysis contributes to biochar production (Oyedun et al., 2013; Waheed et al., 2013; Williams and Besler, 1996).

3.2.3. Effect of heating rate on bio-oil properties

The effects of heating rate on the basic properties of bio-oil are shown in Table 2. The pH value and viscosity of the bio-oil change little, whereas water content slightly decreases with increasing heating rate. The carbon content decreases, whereas oxygen content increases with increasing heating rate. Nitrogen, hydrogen, and sulfur contents barely change.

The water content of bio-oil reaches 62.8–69.5%. This water partly comes from a small amount of bound water in moso bamboo and partly from the thermochemical reactions of cellulose, hemicellulose, and lignin. The water content of the bio-oil obtained from slow pyrolysis is higher than that of the bio-oil obtained from fast pyrolysis (typical fast pyrolysis conditions: 500 °C, residence time <2 s) (Bridgwater, 2012; Lu et al., 2009; Xiao et al., 2007). This is because the volatiles in the second cracking are very significant in slow pyrolysis. On one hand, the internal volatile go through a transport diffusion process to reach the surface of the sample, where it is released. The secondary cracking of the volatile reaction in the diffusion process produces water and small-molecule non-condensable gases. On the other hand, the residence time of the volatile in the pyrolysis furnace is lengthy, and the carbonized samples and the alkali metal content in ash can also catalytically volatilize some small-molecule substances.

Bio-oil is very complex, containing hundreds of compounds. Table 3 lists 21 compounds with high peak area% in GC/MS. It is worth noting that the sum of the total peak area% is less than 100%, which due to the unidentified compounds on the ion chromatograms. Acetic acid and phenolic compounds are found the main organic components in bio-oil. It can be seen from Table 3 that the heating rate does not change the bio-oil components, but affects the relative contents of the components. The relative contents of small-molecule components slightly decrease with increasing heating rate, whereas the relative phenolic substance contents slightly increase.

The small-molecule substances in the bio-oil from slow bamboo pyrolysis are higher than those in rapid bamboo pyrolysis in the literature (Muhammad et al., 2012; Ren et al., 2013), probably because the secondary decomposition of volatiles is more efficient in slow pyrolysis given that the residence time of volatiles in the pyrolysis furnace is lengthy. Therefore, different testing methods for pyrolysis have different effects on the products of bamboo pyrolysis.

3.2.4. Effect of heating rate on non-condensable gas

Non-condensable gas contains CO, CO₂, H₂, CH₄, and a small amount of hydrocarbons (C_nH_m). The volume percentages of the

main non-condensable gases are listed in Table 4. It can be observed that CO₂ concentration slightly decreases, whereas there are no clear change trends for H₂, CH₄ and CO concentration. Previous studies have shown that the release of CO₂ and CO is dominant in the early stages of pyrolysis, mainly resulting from cellulose and hemicellulose decompositions (Yang et al., 2007; Yang et al., 2006). Their concentration reduced rapidly above 400 °C, while H₂ and CH₄ gradually increased, mainly from the slow decomposition of lignin.

3.2.5. Effect of heating rate on biochar

The proximate analysis, ultimate analysis, heating value and specific surface area of moso bamboo and biochar are listed in Table 5. The volatile content of biochar is less than 7%, whereas that of bamboo material is as high as 85%. The fixed carbon content of the biochar ranges from 87% to 89%. The volatile content in the biochar tends to decline with the increase of heating rate, whereas ash content obviously increases. The heating value of biochar is high, and the heating rate seems to have little effect on the heating value of biochar.

Heating rate has a certain effect on the specific surface area of the biochar. The specific surface area of the biochar increases from 64 m²/g to 72 m²/g with the increase of heating rate, which shows that increasing the heating rate helps increase the specific surface area of the biochar.

4. Conclusions

The heating rate was found to significantly affect the pyrolysis behaviors of moso bamboo using TG analysis as well as the products properties using a fixed bed pyrolysis reactor. The temperature gradients in the sample and the secondary decomposition of volatiles are more efficient in the fixed bed pyrolysis reactor than TG analysis. Increasing heating rate increases the temperature range of devolatilization stage, activation energy values, relative phenolic substance contents of bio-oil, CH₄ concentrations in non-condensable gas, and specific surface area of biochar, whereas it decreases biochar yield, viscosity and water content of bio-oil and CO₂ concentration.

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